

UDC 666.3.022.66

## RHEOLOGICAL PROPERTIES OF SLIPS BASED ON POLYMINERAL CLAYS WITH ELECTROLYTE ADDITIVES

Yu. A. Klimosh<sup>1</sup> and I. A. Levitskii<sup>1</sup>

Translated from *Steklo i Keramika*, No. 11, pp. 19 – 22, November, 2004.

The effect of various electrolytes (soda ash, water glass, sodium tripolyphosphate, coal-alkali reactant) as well as their combinations on the rheological properties and electrokinetic potential of ceramic slips for souvenir bottle production based on polymineral clays from Belarus is investigated. It is established that the maximum liquefying of ceramic suspensions is reached under the joint effect of a combination of electrolytes, due to the simultaneous impact of cation exchange and physical adsorption of anions in the system.

Production of ceramics by casting is widely applied in the ceramic industry for making household and fancy majolica, porcelain, and faience products (vases, tea and coffee sets, bottles for pouring alcoholic beverages, etc.).

Since majolica products are usually made from low-grade low-melting clays that have poor liquescence, casting ceramic slip into gypsum molds encounters certain difficulties, namely, poor liquescence and, accordingly, high thickening coefficients.

The rheological properties and aggregate stability of ceramic slips are responsible for their technological properties (mobility, casting rate, degree of filling of gypsum molds) and the physicomachanical properties of finished products (porosity, strength, moisture impermeability, etc.).

Slips with minimum moisture should be easily transported via a slip pipeline, have good filtration properties, and at the same time should not stratify under protracted storage, or contain gas bubbles, or foam in casting [1].

It is known that the rheological properties of casting slip to a large extent are determined by a number of factors: slip composition, solid phase dispersion, solid particle shape, extent of chemical interaction between the solid and liquid phases, low viscosity of the liquid phase, degree of solubility of the solid phase in the liquid one, capacity for dissolving electrolyte, etc.

One of the most effective methods for controlling the rheological properties and the aggregate stability of such suspensions is using liquefying additives (electrolytes) whose effect is based on ion-exchange processes occurring on the surface of mineral particles of the slip.

The most frequently used electrolytes are various sodium salts, which dissociate in the slip and affect the sorbed complex. When an electrolyte is added to a slip with prevalence

of  $\text{Ca}^{2+}$  in its exchange complex,  $\text{Na}^+$  cations, whose adsorption energy is lower than that of  $\text{Ca}^{2+}$ , replace  $\text{Ca}^{2+}$  cations in the sorbed complex, initially in the diffusion layer and afterwards in the surface layer. The replacement of  $\text{Ca}^{2+}$  cations by monovalent  $\text{Na}^+$  increases the thickness of the diffuse shell of the micelles, the electrokinetic potential of the system, and the looseness of the slip structure [2]. Furthermore, liquescence depends not only on cations, but on anions as well, which participate in the ion-exchange processes and replace water molecules adsorbed on the surface of clay particles, which contributes to thinning the slip.

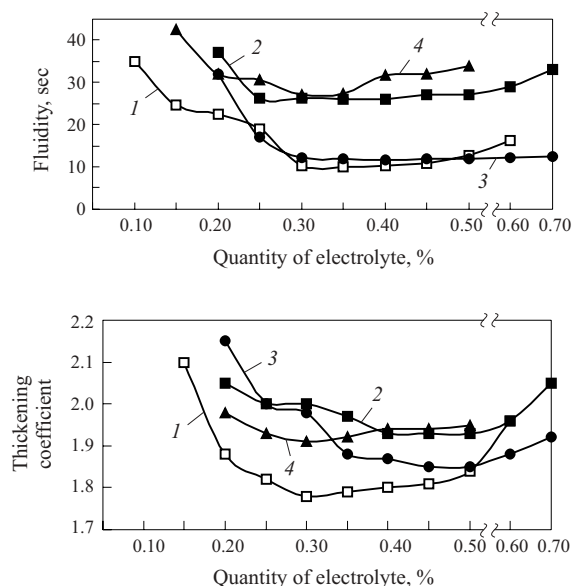
The impact of electrolyte on the state of the slip can take one of three directions: stabilization of the suspension, liquefying the slip, or slip thickening.

A clay suspension is stabilized in the case when electrolyte is introduced in a smaller quantity than the quantity required for a total saturation of the adsorption complex, i.e., a complete replacement of adsorbed cations by electrolyte cations. Water mechanically fixed by argillaceous aggregates is released and the quantity of loosely fixed water increases, although liquescence does not yet occur. At this stage the suspension becomes stabilized under the effect of electrolytes.

After a further increase in the quantity of electrolyte the slip liquefies as loosely bound water transforms into free water thinning the slip. A further addition of electrolyte leads to the thickening of suspension, since thinned aqueous shells cannot prevent clay particles from approaching each other. The viscosity of the slip increases, since emerging aggregates capture a part of free water [1].

The capacity of clay for the adsorption of cations depends on its cation exchange capacity (the maximum quantity of a certain cation that can be adsorbed by the given clay).

<sup>1</sup> Belarus State Technological University, Minsk, Belarus.



**Fig. 1.** Dependence of slip fluidity and thickening coefficient on the type and quantity of electrolyte: 1)  $\text{Na}_3\text{P}_3\text{O}_{10}$ ; 2)  $\text{Na}_2\text{CO}_3$ ; 3)  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 4) CAR.

The liquefying effect of individual agents and complex electrolytes has been investigated. The maximum effective quantity of electrolytes for each particular slip is selected individually.

In the present study we analyze a ceramic slip used in the production of articles with a large wall thickness and a narrow neck. This imposes high technological requirements on the slip, such as good fluidity and low thickening coefficients (1.4 – 1.8).

The material components of the slip considered include low-melting clays from the Gaidukovka (30%) and Lukoml' (30%) deposits in Belarus and also Latnenskoe refractory clay, nepheline-sienite, glass granulate, and high-alumina chamotte, introduced 10% each. To improve the flow properties, traditional electrolytes are used: soda ash  $\text{Na}_2\text{CO}_3$ , water glass  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ , sodium tripolyphosphate  $\text{Na}_3\text{P}_3\text{O}_{10}$ , and the coal-alkali reactant (CAR consists of alkali humates representing salts of aromatic oxycarbon acids containing carboxyl, carbonyl, and metaxyl groups), which are introduced into a mixture during milling (above 100%) separately or in combinations. The slip moisture was 45%, its density was  $1700 \text{ kg/m}^3$ , and the pH was 8 – 9, as a rule, depending on the type and quantity of electrolyte.

The change in the viscosity and the thickening coefficient of the slip containing different quantities of electrolyte was estimated based on the efflux time from an Engler viscosimeter funnel after 30 sec and 30 min exposure.

The initial suspension is a viscous disperse system with a structured flow. After a required quantity of electrolyte is introduced, the structured flow gradually transforms into Newtonian flow.

It is known that the rheological properties of casting slips to a great extent depend on the quantity and the mineral type of argillaceous material. Slips based on montmorillonite-bearing clays have increased thixotropy, which significantly complicates the casting process. The unsatisfactory rheological properties of these slips are the result of an increased quantity of strongly bound water localized in the inter-packing spaces of montmorillonite. This leads to the swelling of montmorillonite and thickening of the slip [3].

According to GOST 21216.0-93, clay from the Gaidukovka deposit is low-melting, moderately plastic, medium-disperse, of low-temperature sintering, and belongs to the kaolinite-montmorillonite-hydromica group of clays. Clay from the Lukoml' deposit is low-melting, medium-plastic, semi-acid, highly disperse, of low-temperature sintering, and belongs as well to the kaolinite-montmorillonite-hydromica group of clays.

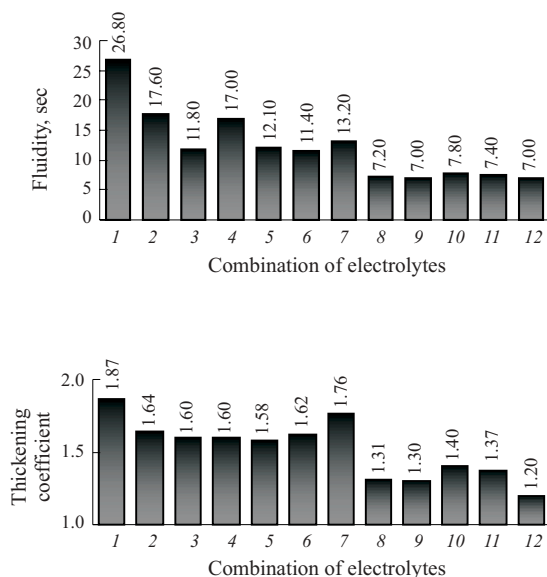
Figure 1 shows the dependence of slip fluidity and thickening coefficient on the type and quantity of electrolyte. It can be seen that introducing each electrolyte separately has a low effect. Thus, the introduction of 0.3 – 0.6% water glass sharply improves fluidity; however, the slip thickening coefficient remains sufficiently high: 1.93 – 1.95. The thinning of the suspension, apart from the effect of  $\text{Na}^+$  cation, is due to the formation of non-dissociating  $\text{CaSiO}_3$  compound that precipitates. At the same time, the hydrate shell is released and thus increased the relative quantity of free mobile water. Furthermore, the liquefying effect of water glass is related to the formation of colloid silicic acid due to its hydrostatic decomposition in water. The acid is adsorbed on the surface of clay particles and the released water perceptibly liquefies the slip [2].

A similar situation is observed when sodium tripolyphosphate is used as electrolyte. The best efflux time (10 – 11 sec) is observed upon introducing 0.30 – 0.45% sodium tripolyphosphate. The thickening coefficient in this case is within the limit of 1.8.

The use of soda ash and the CAR as individual electrolytes has low efficiency, since the fluidity of the slip is not much improved. The high values of the thickening coefficient of slips using these electrolytes point to a low effect of their individual action.

A somewhat different situation is observed using combinations of electrolytes (Fig. 2). The efflux time and the slip thickening coefficient in joint use of soda ash and water glass decrease compared to the same additives introduced separately. The thickening coefficient decreases to 1.6 and the fluidity to 12 sec. However, in the course of settling the slip loses some of its fluidity; therefore, its applicability in casting complex-shaped articles is limited.

Joint application of water glass, soda ash, and sodium tripolyphosphate or water glass. Soda ash, and CAR even more perceptibly decreases the thickening coefficient (to 1.30 – 1.37) and the efflux time (to 7.2 – 7.8 sec). However, testing showed that the discharge of this slip through a narrow neck in casting complex-shaped thick-walled articles is



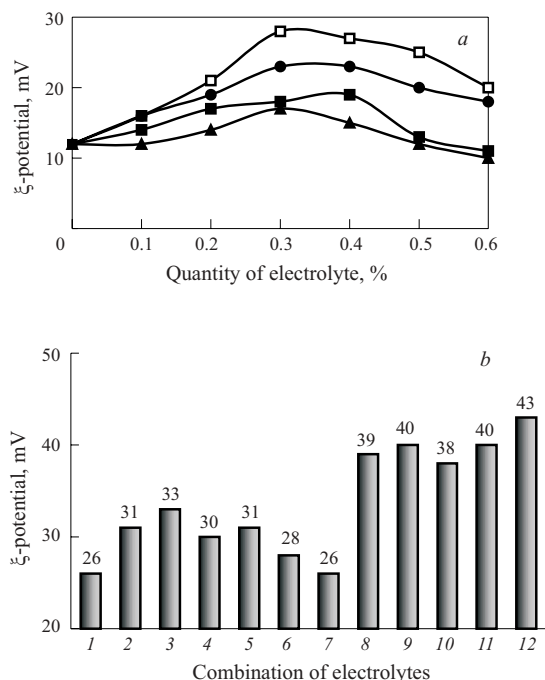
**Fig. 2.** Dependence of fluidity and slip thickening coefficient on the type of combined additive: 1) 0.1%  $\text{Na}_2\text{CO}_3$  + 0.1%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 2) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.1%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 3) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.15%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 4) 0.3%  $\text{Na}_2\text{CO}_3$  + 0.1%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 5) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.2%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 6) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.3%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 7) 0.1%  $\text{Na}_2\text{CO}_3$  + 0.2%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ; 8) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.15%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$  + 0.05%  $\text{Na}_5\text{P}_3\text{O}_{10}$ ; 9) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.15%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$  + 0.1%  $\text{Na}_5\text{P}_3\text{O}_{10}$ ; 10) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.15%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$  + 0.03% CAR; 11) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.15%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$  + 0.05% CAR; 12) 0.2%  $\text{Na}_2\text{CO}_3$  + 0.15%  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$  + 0.05%  $\text{Na}_5\text{P}_3\text{O}_{10}$  + 0.03% CAR.

impeded. This negative effect disappears when a combination of four electrolytes is used: water glass – soda ash – sodium tripolyphosphate – CAR in the amount of 0.20 – 0.15 – 0.05 – 0.03%, respectively.

The high liquefying effect of sodium tripolyphosphate is due to the adsorption of polyphosphate ions on the boundary between oxygen-silicon tetrahedral layers, which is due to the similar structure and size of tripolyphosphate anions and the silicon-oxygen tetrahedra of argillaceous minerals. Furthermore, the geometrical proportions of polyphosphate ions facilitate their denser packing in the structural lattice of water [4]. The carboxyl, carbonyl, and metaxyl groups contained in the CAR as well facilitate the adsorption of its active part on clay particles [5].

The improvement of the rheological characteristics of slip using electrolytes is undoubtedly related to the changing electrokinetic potential of the system. Short-range attraction forces act between particles in suspensions, as well as electrostatic repulsion forces caused by like charges on particle surfaces. The work performed on joining two charged particles depends on their electric potentials. The larger the potentials, the greater the work needed to bring the particles together and the less probable their aggregation [2].

The value of electrokinetic potential  $\xi$  on the boundary between a particle migrating together with adsorbed cations



**Fig. 3.** Dependence of the  $\xi$ -potential on the type and content of individual (a) and combined (b) electrolytes:  $\square$ )  $\text{Na}_5\text{P}_3\text{O}_{10}$ ;  $\blacksquare$ )  $\text{Na}_2\text{CO}_3$ ;  $\bullet$ )  $\text{Na}_2\text{O} \cdot 2.8\text{SiO}_2$ ;  $\blacktriangle$ ) CAR; other notations same as in Fig. 2.

and its hydrate shell and the immobile water layer was determined based on the electrophoresis velocity.

The studies demonstrated that the ceramic slip has a slight negative charge on its surface as a consequence of the diffusion of exchange cations from the solid phase surface into the solution, which is corroborated by the slightly negative value of the  $\xi$ -potential.

It can be seen from Fig. 3 that the dependence of the  $\xi$ -potential on electrolyte content agrees with the fluidity curves: the maximum  $\xi$ -potential value corresponds to the minimum slip viscosity. Thus, the maximum values of  $\xi$ -potential are observed upon introducing 0.3 – 0.4% sodium tripolyphosphate and water glass (28 and 23 mV, respectively). The use of soda ash and the coal-alkali reactant as individual electrolytes is not effective in view of their low liquefying effect, which is confirmed by the  $\xi$ -potential values. When the electrolyte content becomes more than 1.5 – 2 times higher than the adsorption capacity, flocculation of the clay takes place. At the same time, the quantity of mechanical trapped water and the viscosity grow.

The introduction of a combined electrolyte increases the absolute value of the  $\xi$ -potential more significantly than individual introduction of either electrolyte. Electrolyte combinations 9, 11, and 12 (Fig. 3) exhibit the maximum  $\xi$ -potential values equal to 40 – 43 mV, which agrees with the thickening coefficient and fluidity values. The optimum combination of electrolytes presumably contributes to additional

electrostatic repulsion and, accordingly, improves the rheological parameters of clay suspensions.

Another very important factor affecting the flow properties of slips and the possibility of their application in the industry is the dependence of slip fluidity on its temperature. This is especially topical for winter periods, when the temperature in production shops decreases to 5–7°C. In this context, we investigated the variation in the fluidity of the slip with the optimum combination of electrolytes (12) depending on its temperature. The optimum efflux time (6–7 sec) was observed in suspensions within a temperature interval of 15–30°C. Slips with a temperature below 10°C have slightly inferior parameters. At 10°C the slip has higher fluidity values (8–10 sec) and a higher thickening coefficient (1.46).

The flow properties of slip also depend on the hardness of water used. When water hardness grows over 4.5–5.0 mmole · equ/liter of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, the fluidity and aggregate stability of the suspension sharply deteriorate.

Thus, the use of individual thinners in slips based on polymineral clays from Belarus has little effect; it is more effective to use complex electrolytes. The maximum thinning of the ceramic suspension under the joint effect of combined

electrolytes is presumably due to two parallel processes occurring in the system: cation exchange and physical adsorption of anions.

The optimum combination of electrolytes (12) has been tested in industrial conditions at the Belkhudozhkeramika Company and has been included in the production of souvenir bottles for alcoholic beverages.

## REFERENCES

1. I. I. Moroz, *Technology of Porcelain and Faience Articles* [in Russian], Stroiizdat, Moscow (1984).
2. N. M. Bobkova, E. M. Dyatlova, and T. S. Kunitskaya, *General Technology of Silicates* [in Russian], Vysshaya Shkola, Minsk (1987).
3. M. K. Gal'perina and N. V. Kolyshkina, "Improvement of rheological and technological properties of casting slips by introducing organic liquefiers," *Steklo Keram.*, No. 7, 18 (1984).
4. A. L. Reznik, L. V. Komolaeva, A. I. Ovchinnikova, et al., "Slip with decreased moisture based on polymineral clays from the Transcarpathian Region," *Steklo Keram.*, No. 12, 17–18 (1984).
5. N. G. Shcherbakova, N. S. Belostotskaya, and T. B. Varlakhina, "New thinners for porcelain slips," *Steklo Keram.*, No. 6, 19–21 (1986).